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# KINETICS OF THE REACTION OF CO<sub>2</sub> WITH THE STERICALLY HINDERED AMINE 2-AMINO-2-METHYLPROPANOL at 298 K

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**Abstract**—Absorption rates of CO<sub>2</sub> into aqueous solutions of the sterically hindered amine AMP (2-amino-2-methylpropanol), under reaction-controlled conditions were measured. The experiments were carried out in a stirred vessel with a smooth horizontal interface. The results were interpreted in terms of the zwitterion mechanism for the reaction of CO<sub>2</sub> with primary or secondary amines as originally proposed by Caplow (1968, *J. Am. chem. Soc.* **90**, 6795–6803) and Danckwerts (1979, *Chem. Engng Sci.* **34**, 443–446). The reaction rate constants and the equilibrium constant describing the stability of the carbamate of AMP were determined by fitting numerically calculated absorption rates to the experimentally observed ones. These constants were compared with data reported for AMP and with those for not sterically hindered amines. The relative values of the reaction rate constants could be explained only partially.

## INTRODUCTION

Alkanolamines have already been used for many years in acid gas treating processes [e.g. Kohl and Riesenfeld (1979)]. The application of sterically hindered amines as an absorbent was originally suggested by Sharma (1964). In the early 1980s this concept was developed by Sartori and Savage (1983) and Savage *et al.* (1984). Recently studies on the absorption rates of CO<sub>2</sub> into sterically hindered amines, specifically AMP, were presented by Chakraborty *et al.* (1986) and Zioudas and Dadach (1986). However no detailed reaction mechanism was presented.

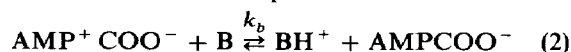
A study on the molecular structure of these amines, using the hard and soft acid–base theory by Chakraborty *et al.* (1988a, b) showed that the instability of the carbamates of these amines is not caused by steric hindrance but by electronic effects caused by the methyl substitutions at the  $\alpha$ -carbon atom, suggesting that the name for this class of amines is in fact incorrect. It was also shown that these electronic effects reduce the basic strength of the amines and their reaction rates in the classical zwitterion mechanism (Caplow, 1968; Danckwerts, 1979) for the reaction of CO<sub>2</sub> with primary or secondary amines. An alternative reaction path in which the activated complex of CO<sub>2</sub> and the amine reacts with OH<sup>−</sup> to give bicarbonate and the free amine was suggested.

Bosch *et al.* (1989) evaluated the results of Chakraborty *et al.* (1986) and Zioudas and Dadach (1986) with the aid of a numerical model which describes the absorption of a gas component accompanied by parallel reversible reactions (Versteeg *et al.*, 1989). Unfortunately only few of the relevant experimental physico-chemical constants and mass transfer parameters necessary for the absorption model were presented in the original publications. Therefore estimated values had to be used. In spite of this lack of information it was shown that the CO<sub>2</sub> absorption rates observed in sterically hindered amine solutions can probably be explained satisfactorily with the zwitterion mechanism, so no new mechanism is necessary.

In order to verify this hypothesis new CO<sub>2</sub> absorption data for aqueous AMP solutions have been collected and will be presented in this paper. The experimental technique developed by Blauwhoff *et al.* (1984) and Versteeg and van Swaaij (1988a) was used. The solubility and diffusivity of CO<sub>2</sub> were determined by means of the CO<sub>2</sub>–N<sub>2</sub>O analogy (Laddha *et al.*, 1981) and a modified Stokes–Einstein relation (Versteeg and van Swaaij, 1988b). The AMP concentration was varied between 200 and 2400 mol m<sup>−3</sup>.

## REACTION MECHANISM

The zwitterion mechanism is generally accepted for the description of the reaction between CO<sub>2</sub> and primary or secondary amines. It consists of two steps (Caplow, 1968; Danckwerts, 1979). In the first step (1) CO<sub>2</sub> reacts with AMP to form an intermediate, the zwitterion. In the second step (2) the zwitterion is deprotonated by the bases present in the solution. According to Blauwhoff *et al.* (1984) the rate expression for this reaction (3) can be derived from the assumption of a pseudo-steady state for the zwitterion concentration. It should be noted that the contributions of all the bases present in the solutions to the deprotonation step should be taken into account. In aqueous solutions this includes not only the amine but also water and hydroxyl ions.



$$r = \frac{k_2 [\text{CO}_2] [\text{AMP}]}{1 + \frac{k_{-1}}{\sum k_b [\text{B}]}} \quad (3)$$

The equilibrium constant (5) for the overall reaction of CO<sub>2</sub> with AMP (4) is extremely low, which is

typical for sterically hindered amines. Versteeg *et al.* (1989) have demonstrated that the conditions for absorption to occur in the pseudo-first-order regime are more severe for such highly reversible reactions than for irreversible ones [e.g. Danckwerts (1970)]. Moreover, this high reversibility can prevent fulfilment of the conditions for pseudo-first-order reaction at all. Nevertheless, it may be possible to determine the reaction kinetics from absorption rates if an absorption model which takes the reversibility into account is used to interpret the experimental results.



$$K_{\text{eq}} = \frac{[\text{AMPH}^+][\text{AMPCOO}^-]}{[\text{AMP}]^2[\text{CO}_2]} \quad (5)$$

Moreover, with AMP the situation is even more complicated as in its aqueous solutions  $\text{CO}_2$  also reacts directly with the hydroxyl ion (6). Usually, for other amines the contribution of this hydration reaction to the absorption rate is very low (Blauwhoff *et al.*, 1984). In this case the contribution might be important, because the reaction to carbamate proceeds to a much lower conversion, and possibly with a lower reaction rate.



For the system  $\text{CO}_2$ -aqueous AMP solutions, presently under investigation, two parallel reversible reactions [(4) and (6)] should be considered, which also interact due to the equilibrium reaction (7). For such a complicated reaction mechanism no generally applicable analytical expressions for the absorption rate are available. Therefore a numerical solution of the model for mass transfer with chemical reactions is necessary. Details of the numerical method used have been presented elsewhere (Versteeg *et al.*, 1989; Bosch *et al.*, 1989).



## RESULTS AND DISCUSSION

In Tables 1 and 2 experimental data on the viscosity and the solubility of  $\text{N}_2\text{O}$  in AMP solutions at 298 K are presented. The viscosities were measured with Ubbelohde viscosimeters. The solubility was measured in the way described by Versteeg and van Swaaij (1988b). The diffusivities of the species in the liquid were estimated in the way described by Bosch *et al.* (1989) and Bosch (1989). The value of the liquid phase mass transfer coefficient was calculated from the relation determined by Versteeg *et al.* (1987) for a stirred cell with similar geometry. The rate of hydration of  $\text{CO}_2$  (8) was obtained from Pinsent *et al.* (1956) (9). The relevant equilibrium constants for 298 K were presented in Bosch *et al.* (1989). Because only an upper limit of the equilibrium constant describing the stability the carbamate of AMP ( $K_c$ ) is available (Chakraborty *et al.*, 1986), this parameter also has to be obtained from the experiments.

$$r = k_{\text{OH}} [\text{OH}^-] [\text{CO}_2] \quad (8)$$

Table 1. Viscosity of AMP solutions at 298 K

$c_{\text{AMP}}$ (mol m <sup>-3</sup> )	$\eta$ ( $\times 10^{-3}$ Pas)
0	0.8904
258	0.95
511	0.98
769	1.06
999	1.16
1181	1.25
1288	1.30
1394	1.36
1576	1.44
1783	1.58
2119	1.76
2265	1.95
2484	2.21

Table 2. Solubility of  $\text{N}_2\text{O}$  in AMP solutions at 298 K

$c_{\text{AMP}}$ (mol m <sup>-3</sup> )	$m_{\text{N}_2\text{O}}$
0	0.623
235	0.62
452	0.62
622	0.61
793	0.61
1014	0.61
1186	0.59
1415	0.59
1612	0.59
1816	0.57
1989	0.56
2255	0.55
2499	0.53

$$\log k_{\text{OH}} = 10.635 - \frac{2895 \text{ K}}{T} \quad (9)$$

The reverse-reaction rates were calculated by assuming that the equilibrium constants are equal to the ratio of the forward and reverse reaction rates, as is the case for equilibrium conditions.

From the observed decrease of pressure with time (not exponential) it was concluded that for none of the absorption experiments did simple pseudo-first-order conditions prevail, even though at very low gas phase concentrations (100 Pa) the conditions for a pseudo-first-order irreversible reaction were met. This is probably due to the reversibility of the reaction, as indicated above. Versteeg *et al.* (1989) showed that for reactions with very low equilibrium constants the observed behaviour can be predicted theoretically. Therefore it was not possible to derive the reaction rates directly from the absorption experiments by assuming a pseudo-first-order reaction.

With the aid of the numerically solved film model for absorption according to Bosch *et al.* (1989), and by

Table 3. Results of absorption experiments at 298 K

No.	$c_{\text{am}}$ (mol m <sup>-3</sup> )	$k_L$ ( $\times 10^{-5}$ m s <sup>-1</sup> )	$c_{\text{H}_2\text{O}}$ ( $\times 10^3$ mol m <sup>-3</sup> )	$D_{\text{CO}_2}$ ( $\times 10^{-9}$ m <sup>2</sup> s <sup>-1</sup> )	$m_{\text{CO}_2}$ ( $\times 10^{-1}$ mol m <sup>-3</sup> )	Higher CO <sub>2</sub> pressure						Lower CO <sub>2</sub> pressure			
						$c_{\text{CO}_2, \text{g}}$ ( $\times 10^{-1}$ mol m <sup>-3</sup> )	$c_{\text{CO}_2, \text{L}, \text{f}}$ (mol m <sup>-3</sup> )	$J_{\text{CO}_2, \text{exp}}$ ( $\times 10^{-4}$ mol m <sup>-2</sup> s <sup>-1</sup> )	$J_{\text{CO}_2, \text{sim}}$ ( $\times 10^{-4}$ mol m <sup>-2</sup> s <sup>-1</sup> )	$J_{\text{CO}_2, \text{exp}}/J_{\text{CO}_2, \text{sim}}$	$c_{\text{CO}_2, \text{g}}$ ( $\times 10^{-1}$ mol m <sup>-3</sup> )	$c_{\text{CO}_2, \text{L}, \text{f}}$ (mol m <sup>-3</sup> )	$J_{\text{CO}_2, \text{exp}}$ ( $\times 10^{-5}$ mol m <sup>-2</sup> s <sup>-1</sup> )	$J_{\text{CO}_2, \text{sim}}$ ( $\times 10^{-5}$ mol m <sup>-2</sup> s <sup>-1</sup> )	$J_{\text{CO}_2, \text{exp}}/J_{\text{CO}_2, \text{sim}}$
1	202	2.40	54.4	1.89	8.42	4.84	0.85	1.46	1.44	0.99	1.35	0.91	4.22	4.24	1.00
2	206	1.93	54.4	1.89	8.42	6.72	0.57	1.97	1.91	0.97	1.08	0.64	3.58	3.48	0.97
3	298	1.71	54.0	1.87	8.40	6.05	2.05	1.87	1.89	1.01	0.54	2.12	1.81	1.87	1.03
4	308	2.14	53.9	1.86	8.40	4.44	0.73	1.79	1.72	0.96	1.35	0.80	5.41	5.49	1.01
5	400	1.86	53.5	1.84	8.38	6.05	2.89	2.27	2.29	1.01	0.94	2.96	3.78	3.81	1.01
6	401	2.16	53.5	1.84	8.38	4.44	0.64	1.96	2.02	1.03	1.21	0.69	5.58	5.79	1.04
7	816	1.70	51.5	1.67	8.27	6.19	0.63	3.93	3.92	1.00	1.35	0.72	8.96	9.08	1.01
8	810	1.58	51.5	1.68	8.27	4.84	1.92	3.07	2.97	0.97	0.94	1.97	6.27	6.07	0.97
9	1556	1.24	48.0	1.33	7.93	7.26	2.25	5.39	5.62	1.04	2.15	2.31	16.7	17.5	1.05
10	1487	1.29	48.3	1.36	7.97	6.46	0.59	5.20	5.10	0.98	1.61	0.67	13.4	13.4	1.00
11	2310	1.02	44.4	1.02	7.42	3.63	0.73	3.23	3.15	0.97	1.08	0.78	9.64	9.61	1.00
12	2373	0.99	44.1	0.99	7.36	2.02	2.93	1.72	1.73	1.01	0.54	2.95	4.66	4.67	1.00

fitting the absorption data both the reaction rate constants and the carbamate stability constant were calculated from the absorption data. For each experiment the absorption rate was determined at a very low and a moderately low pressure. The experimental data thus obtained and the physico-chemical constants used in the evaluation of the experiments are collected in Table 3.

The values of the resulting constants are given in Table 4. With these constants the observed absorption rates can be calculated with a standard deviation of 2.5%. Because the concentration of OH<sup>-</sup> was very low in the experiments the rate constant for its contribution to the deprotonation step (2) could not be evaluated accurately. Its contribution was therefore neglected. In Fig. 1 the ratio of the calculated and the observed absorption rates is shown as a function of the amine concentration.

The reaction rate constant for the formation of the zwitterion,  $k_2$ , cannot be calculated accurately because the deprotonation is the main rate-determining step. Moreover, it is not possible to measure  $k_2$  more precisely by increasing the AMP concentration as the overall deprotonation rate constant is two orders of magnitude lower.

Similar to  $k_2$  the value of  $K_c$  is not very accurate, due to the fact that the experiments were carried out with very low CO<sub>2</sub> liquid loadings. Therefore the rate of the reverse reaction is very low and so the overall reaction rate near the interface is mainly determined by the forward reaction. Because of this inaccuracy the carbamate stability constant should preferably be obtained from equilibrium experiments [e.g. Chan and Danckwerts (1981)].

In Figs 2 and 3 a typical example of the numerically calculated concentration profiles according to the absorption model is given. A certain limitation due to diffusion of AMP and its reaction products is obvious from the gradients in their concentrations. This diffusional limitation of AMP species coincides well with the observation that for the absorption of CO<sub>2</sub> the pseudo-first-order regime was never reached. The hydration of CO<sub>2</sub> is very important for the overall absorption rate. The gradient in the concentration of HCO<sub>3</sub><sup>-</sup> seems to indicate a contribution of this reaction. However, the acid-base equilibrium between HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> causes the CO<sub>3</sub><sup>2-</sup> concentration to have a gradient in the other direction. So no net CO<sub>2</sub> transport by these species occurs. The gradients only

Table 4. Values of constants derived from experiments

Constant	Value	Estimated inaccuracy (%)
$k_2$	$10^1 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	100
$k_2 k_{\text{AMP}}/k_{-1}$	$1.27 \times 10^{-4} \text{ m}^6 \text{ mol}^{-2} \text{ s}^{-1}$	10
$k_2 k_{\text{H}_2\text{O}}/k_{-1}$	$8.36 \times 10^{-6} \text{ m}^6 \text{ mol}^{-2} \text{ s}^{-1}$	10
$K_c$	$4.8 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$	20

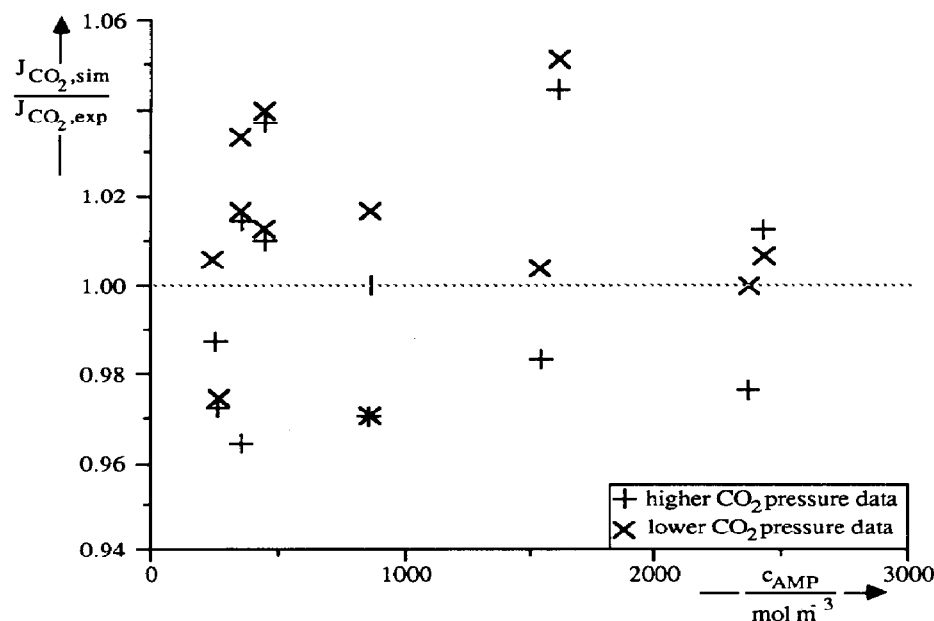


Fig. 1. Comparison of experimental and simulated absorption rates.

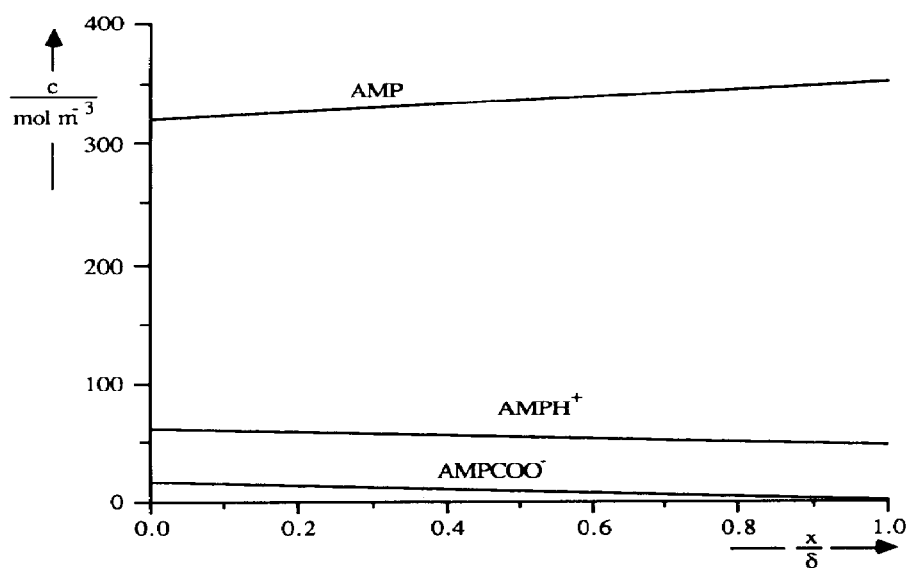


Fig. 2. Calculated concentration profiles for the numerical film model solution (experiment 5, higher  $\text{CO}_2$  pressure).

serve to transport protons produced in the reaction of  $\text{CO}_2$  with AMP, which are therefore only partly transported as  $\text{AMPH}^+$ .

In Fig. 4 the composition of the liquid compared to equilibrium (5) is shown. It is clear from Fig. 4 that the reaction can not be treated as irreversible. Only very near to the interface does a substantial deviation from equilibrium exist. In fact in most of the film the  $\text{CO}_2$  concentration is slightly lower than the equilibrium concentration, due to the consumption of  $\text{CO}_2$  by the

hydration reaction. This causes reactions (1) and (2) to proceed slightly in the reverse direction.

Chakraborty *et al.* (1986) studied absorption rates of  $\text{CO}_2$  into AMP solutions in a pressure decrease cell. From the observed first-order relation between the reaction rate and both the  $\text{CO}_2$  and the AMP concentration they concluded that AMP acts as a catalyst for the hydration of  $\text{CO}_2$ , and that the rate-determining step in this catalytic route is the formation of an intermediate by the reaction of  $\text{CO}_2$

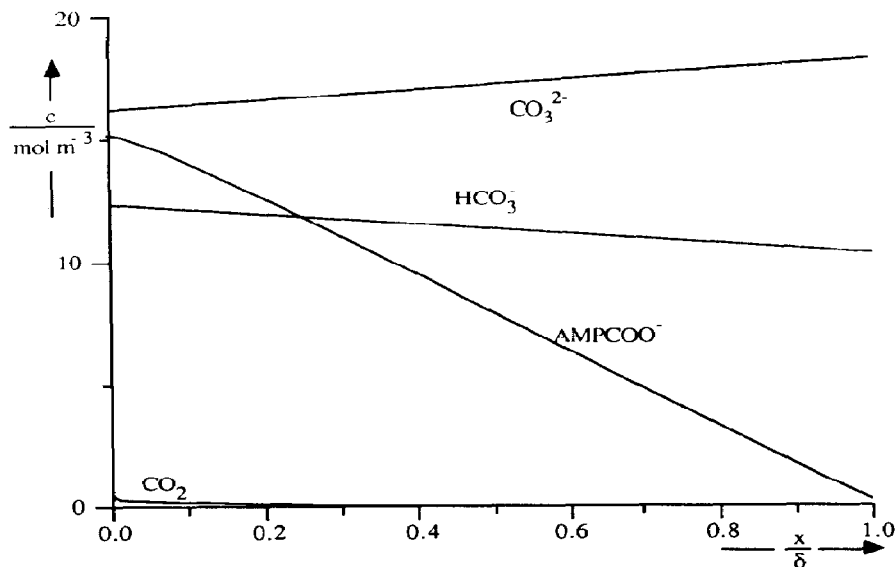


Fig. 3. Expansion of Fig. 2 for low concentrations.

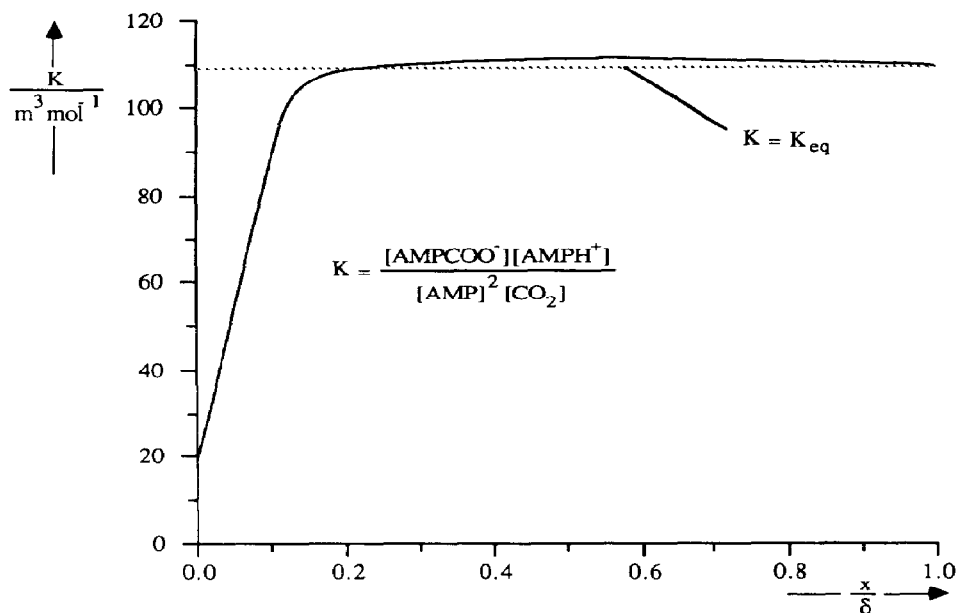


Fig. 4. Liquid composition for the film model solution.

with the amine. The rate constant for this step should be of the order of  $0.1 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The classical zwitterion mechanism for the reaction of CO<sub>2</sub> with primary or secondary amines was not taken into account by Chakraborty *et al.* (1986), because the carbamate of AMP is very unstable. The mechanism suggested by Chakraborty *et al.* (1986) cannot explain the deviations from pseudo-first-order behavior observed in this study, however, while the present mechanism can. The present experimental results would lead to a pseudo-first-order reaction rate constant of

about  $0.4 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , which is of the magnitude suggested by Chakraborty *et al.* (1986).

The value of  $K_c$  derived from our work is well below the upper limit considered possible by Chakraborty *et al.* (1986) ( $10^{-4} \text{ m}^3 \text{ mol}^{-1}$ ). The value of  $k_2$  can be calculated within its experimental accuracy by the relation of Versteeg and van Swaaij (1988a) for primary and secondary alkanolamines. Values for the deprotonation constants are only available for DIPA (Versteeg and van Swaaij, 1988a) and DEA (Versteeg and Oyeveaar, 1989). These values are summarized in

Table 5. Comparison of rate constants for DEA, DIPA and AMP

Constant	Amine		
	DIPA	DEA	AMP
$K_a$ (mol m <sup>-3</sup> )	$1.29 \times 10^{-6}$	$1.12 \times 10^{-6}$	$1.95 \times 10^{-7}$
$K_c$ (m <sup>3</sup> mol <sup>-1</sup> )	$4.7 \times 10^{-3}$	$3.4 \times 10^{-3}$	$4.8 \times 10^{-5}$
$k_2 k_{H_2O}/k_{-1}$ (m <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup> )	$0.84 \times 10^{-6}$	$1.71 \times 10^{-6}$	$8.36 \times 10^{-6}$
$k_2 k_{Am}/k_{-1}$ (m <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup> )	$1.98 \times 10^{-4}$	$7.07 \times 10^{-4}$	$1.27 \times 10^{-4}$
$\frac{k_{Am}}{k_{H_2O}}$	236	221	15

Table 5 together with those for AMP. Explanation of the differences between the rate constants for the various amines is difficult because of their compound nature. These rate constants consist of a term ( $k_2/k_{-1}$ ) representing the stability of the zwitterion relative to CO<sub>2</sub> and AMP, and a term ( $k_b$ ) describing the rate of the deprotonation step itself. Versteeg and van Swaaij (1988a) have demonstrated that  $k_2$  increases with the basic strength of the amine. Probably the ratio  $k_2/k_{-1}$  depends on both the basic strength and the stability of the carbamate, so the dependence of the product ( $k_b k_2/k_{-1}$ ) on the amine properties is hard to determine.

Blauwhoff *et al.* (1984) showed that for a single amine there is a relation between the strength of the base and its rate constant for deprotonation. This behaviour is also observed in the present study in which  $k_{H_2O} < k_{Am}$ . However comparison of the values for the deprotonation rate constants ( $k_b k_2/k_{-1}$ ) for the amines DIPA, DEA and AMP does not give simple and straightforward relations.

In the sequence DIPA–DEA–AMP (Table 5) the values of  $k_{H_2O} k_2/k_{-1}$  increase and also the basic strength of the amine, suggesting a similar relation between  $k_{H_2O} k_2/k_{-1}$  and  $pK_a$  as observed for  $k_2$ . However, for the same sequence such a relation between  $k_{Am} k_2/k_{-1}$  and the  $pK_a$  of the amines does not exist at all.

If the ratio of the two constants ( $k_{Am}/k_{H_2O}$ ) is compared and thus the influence of  $k_2/k_{-1}$  is eliminated, it is evident that  $k_{Am}/k_{H_2O}$  increases with the carbamate stability and decreases with the basic strength of the amine. If steric hindrance were the cause of the low stability of the carbamate of AMP this would imply that the deprotonation of the zwitterion by the amine is more affected by steric hindrance than the deprotonation by water, which would make perfect sense. The results of the study by Chakraborty *et al.* (1988a) have shown that this is probably not a valid argument, and these results should be taken into account in the explanation.

Because DEA and DIPA have substitutions at the nitrogen atom instead of at the  $\alpha$ -carbon in AMP, the effects discussed by Chakraborty *et al.* (1988a) should be even stronger than for AMP. This is in contradiction with their much stabler carbamates, but it does explain their much lower basic strength. The basic

strength in the Brønsted sense is the factor governing the relative values of the rates of the proton removal step (2) for various bases. Probably the zwitterions of amines with a lower basic strength are more easily deprotonated by water, but not by the amines themselves. This would cause the ratio  $k_{Am}/k_{H_2O}$  to increase with basic strength, which is just the opposite of the observed effect.

## CONCLUSION

In the present study the kinetics of the reactions between CO<sub>2</sub> and aqueous solutions have been studied in order to verify that the reaction can be described according to the generally accepted zwitterion mechanism. In order to derive the kinetics from absorption experiments it is necessary to use a numerically solved absorption model which describes absorption accompanied by several parallel chemical reactions. It was not possible to determine the kinetics in the well-known fast-reaction regime with the assumption of a pseudo-first-order reaction derived for irreversible reactions.

The values of the various rate constants and the stability of the carbamate of AMP can be determined with reasonable accuracy. It is not possible to explain the relative values of the rate constants for the deprotonation of the zwitterions for various amines from the molecular structure and the basic strength of the amines.

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## NOTATION

$c$	concentration, mol m <sup>-3</sup>
$D$	diffusion coefficient, m <sup>2</sup> s <sup>-1</sup>
$J$	molar absorption flux, mol m <sup>-2</sup> s <sup>-1</sup>
$k_b$	reaction rate constant for zwitterion deprotonation, m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
$k_L$	liquid phase mass transfer coefficient, m s <sup>-1</sup>
$k_{-1}$	reverse-reaction rate constant, s <sup>-1</sup>
$k_2$	second-order reaction rate constant, m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
$K$	concentration ratio $\{([AMPCOO^-]/[AMPH^+])/([AMP]^2[CO_2])\}$ , m <sup>3</sup> mol <sup>-1</sup>

$K_c$	carbamate stability constant $\{[\text{AMPCOO}^-]/([\text{AMPH}][\text{HCO}_3^-])\}$ , $\text{m}^3 \text{mol}^{-1}$
$K_{eq}$	equilibrium constant $\{([\text{AMPCOO}^-][\text{AMPH}^+])/([\text{AMP}]^2[\text{CO}_2])\}$ , $\text{m}^3 \text{mol}^{-1}$
$K_a$	primary or secondary amine protonation constant $([\text{AMPH}][\text{H}^+]/[\text{AMPH}_2^+])$ , $\text{mol m}^{-3}$
$m$	distribution coefficient (dimensionless solubility), $\text{mol m}^{-3} \text{mol}^{-1} \text{m}^3$
$x$	spatial coordinate, m

#### Greek letters

$\delta$	thickness of laminar film, m
$\eta$	dynamic viscosity, Pa s

#### Subscripts

Am	amine
g	gas
exp	experimental
L	liquid
sim	simulated
t	total

#### Amine abbreviations

AMP	2-amino-2-methylpropanol
DEA	diethanolamine
DIPA	diisopropanolamine

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